Multidimensionally Stimuli-Responsive Phase Transition of Aqueous Solutions of Poly((*N,N*-dimethylamino)ethyl methacrylate) and Poly(*N,N*-dimethyl-*N*-(methacryloyl)ethyl ammonium butane sulfonate)

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ABSTRACT: Free radical polymerization of *N,N*-(dimethylamino)ethyl methacrylate and *N,N*-dimethyl-*N*-(methacryloyloxy)ethyl ammonium butane sulfonate was carried out to prepare PDMAEMA and PDMABS. Proton nuclear magnetic resonance spectroscopy indicated that both PDMAEMA and PDMABS exhibited an electrolyte-responsive conformational dynamics in D_2O of different ionic strength. PDMAEMA, as a polybase, and PDMABS, as a polysulfobetaine, exhibited a series of multidimensional stimuli-responsive phase transition behaviors. Adding NaCl would decrease the phase transition temperature (T_{PT}) of their aqueous mixtures, because of polyelectrolyte effect for PDMAEMA and anti-polyelectrolyte effect for PDMABS, respectively. For PDMAEMA, a low pH would facilitate the dissolution; on the other hand, for PDMABS, a maximum T_{PT} was achieved in neutral media. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3548–3556, 2008

Key words: LCST; UCST; phase transition; pH-dependent; electrolyte-responsive; thermoresponsive

INTRODUCTION

The physicochemical properties of hydrosoluble polymers and their aqueous solutions have attracted much attention from both academia and industry.[1] Typical water-soluble polymers embrace polyacrylamide (PAM), polyacrylic acid (PAAc) and its salts, poly(vinylpyridine) (PVP) and its *N*-alkylated derivatives, poly(ethylene imine) (PEI), polyoxazoline (POXZ), poly((*N,N*-dimethylamino)ethyl methacrylate) (PDMAEMA) and its *N*-alkylated derivatives, poly(ethylene oxide) (PEO), etc. They have been utilized for flocculation, dispersion, stabilization, viscosification, moisture sorption, metal recovery, as well as other application potentials.[1]

The behavior of polymers in a given medium reflects the balance interaction among its own segments and the surrounding molecules.[2,3] For some polymers, their aqueous solutions could undergo observable phase transition in response to the external factors, viz. pH, ionic strength, and temperature.[1] In particular, polyampholytes, i.e. the copolymers of anionic monomers and cationic monomers, could form a homogeneous solution when dissolved in acidic or alkaline aqueous media to achieve a high charge asymmetry, characteristic of common polyelectrolyte.[4–6] However, the phase transition from a solution to an emulsion could be triggered by adjusting the aqueous pH to around isoelectric points (IEP), in which there is no net charge in polyampholytic chains.[4–6] The typical polyampholytes, including poly(acrylic acid)-*co*-poly(vinylpyridine) and poly(acrylic acid)-*co*-poly((*N,N*-dimethylamino)ethyl methacrylate), have been intensively investigated for a detailed understanding on their phase transition and conformational change.[4–8]

Also termed as inner salt,[9] polybetaines, containing both positive and negative charges in individual repeat units, represent another class of water-soluble polymers, in which the phase transition is triggered by ionic strength. When dispersed in electrolyte-free aqueous media, because of the intrachain and interchain electrostatic attraction as well as the hydrophobic interaction of the main chains, polybetaines

assume a globular conformation, and the matrices form a *de facto* cross-linked network, leading to a turbid emulsion. However, such electrostatic attraction could be shielded by the addition of NaCl, leading to a globule-to-coil transition in the chain conformation. As a result, the polybetaine network is disrupted finally to achieve a homogeneous aqueous solution.[10–16]

Although the lower critical solution temperature (LCST)-type phase transition of polystyrene/cyclohexane system has been noted,[17,18] thermoresponsive phase transitions primarily occur and have been investigated in aqueous systems of both nonionic hydrogen-bondable systems and polybetaines. Poly(*N*-isopropylacrylamide) (PNIPAm) is the most popularly studied member of the former class that possess an inverse aqueous solubility upon heating.[3] Hydrogen bonding interaction of amide moieties of PNIPAm with water facilitates its dissolution at lower temperature. Upon heating, enhanced hydrophobic effect of isopropyl moieties and weakened hydrogen bonding reduce the water solubility of PNIPAm. At a certain critical temperature, negative excess entropy of mixing is achieved, favorable to a phase transition from solutions to emulsions. It has also been noted that the phase diagram of aqueous PNIPAm solution is rather flat, indicating that transition temperature of aqueous PNIPAm solution show negligible concentration dependence, helpful to experimentally determine LCST using cloud point measurement, differential scanning calorimetry, light scattering, viscometry, and so on.[3]

On the other hand, this PNIPAm-specific phenomenon has probably given rise to a misunderstanding among many researchers that the phase transition temperature (T_{PT}) equals to the LCST or *vice versa*. In fact, for a given system in which the properties of polymer (chemical structure including MW and MWD, monomer composition, terminal functionality, etc.) and the solvent (chemical nature including composition, pH, ionic strength, etc.) are fixed, LCST has been accordingly specified; while the T_{PT} is, in addition to chemical natures of both the polymer and solvent, additionally, depending on the composition of the polymer/solvent binary system, i.e. the polymer concentration.

Diametrically opposite to aqueous PNIPAm solutions, those of polybetaines exhibit a upper critical solution temperature (UCST)-type phase transition; i.e. they are water-insoluble at lower temperature due to the electrostatic attraction. Heating promotes the water molecules to diffuse into the network, leading to the disruption of the network at a critical temperature. As a result, the solution undergoes an emulsion–dissolution phase transition.[10,11]

Besides PNIPAm, poly((*N*,*N*-dimethylamino)ethyl methacrylate) (PDMAEMA) is also known for its LCST-type phase transition behavior, since the tertiary amine moieties can hydrogen-bond with water, while the gemini methyl groups exert hydrophobic effects. What is more, the amines could undergo *N*-alkylation (quaternization or betainization), to result in cationic polyelectrolytes or zwitterionic polybetaines, respectively. In addition, since PDMAEMA itself could be deemed as a weak polyelectrolyte to a certain extent, the effect of pH and ionic strength of aqueous media may impose significant influence on the phase transition of its aqueous solution. Therefore, the aqueous PDMAEMA systems might exhibit a multidimensional stimuli-responsive behavior. However, there have been few systematic investigations for such a multidimensional stimuli-responsive aqueous polymer mixtures, especially *vis-à-vis* PNIPAm.

In this article, we report on the phase transition behaviors of aqueous solutions of PDMAEMA and poly(*N*,*N*-dimethyl-*N*-(methacryloyloxy)ethyl ammonium butane sulfonate) (PDMABS) prepared from the sulfobetaine derivative of DMAEMA. Both of them were found to exhibit an electrolyte-responsive conformational dynamics using nuclear magnetic resonance spectroscopy. Thus, their phase transition temperature (T_{PT}), as a function of polymer concentration, pH, ionic strength, etc., was studied in-depth. It might help to clarify the multidimensional stimuli-responsive behaviors of both PDMAEMA and polybetaines.

EXPERIMENTAL SECTIONS

Materials

(*N*,*N*-dimethylamino)ethyl methacrylate (DMAEMA) was purchased from Xinyu Fine Chemicals, Wuxi, China. The inhibitor was removed by distillation *in vacuo*. 1,4-butane sultone was from Fengfan Chemical, Wuhan, China. Ammonium persulfate (APS) and 2,2′-azoisobutyrynitrile (AIBN) was from Shanghai Chemical Reagent, Shanghai, China. They were recrystallized before use.

Sulfobetainization of DMAEMA (DMABS)

DMAEMA (0.127 mol) and 1,4-butane sultone (0.125 mol) were added into a 50 mL single-necked round-bottom flask to form a transparent and colorless solution. The solution was sealed to react at room temperature overnight to produce white powders, *N*,*N*-dimethyl-*N*-(methylmethacryloyl ethyl) ammonium butane sulfonate (DMABS). The powders were washed by acetone and recovered by filtration and dried in vacuum overnight. The yield was about 85%.

Homopolymerization of DMAEMA (PDMAEMA)

DMAEMA (63.5 mmol), AIBN (0.3 mmol), tetrahydrofuran (THF, 20 mL) were added into a flask. After sealing, the system was allowed to react at 70°C for 56 h. After the reaction was completed, the PDMAEMA was precipitated in petroleum ether. After being washed by petroleum ether several times, the polymer was dried under reduced pressure at 100°C for about 24 h to yield white blocks.

Homopolymerization of DMABS (PDMABS)

DMABS (34.1 mmol) and APS (0.2 mmol) were added into deionized water (20 mL) to form a colorless solution. The system was allowed to react at 70°C for 24 h. After the reaction, the solution was cooled down to room temperature and poured into acetone. The polymer was recovered by drying in vacuum at about 100°C for overnight to yield white or slightly yellow loose blocks, which are highly hygroscopic when exposed to atmosphere.

Fourier-transform infrared and proton nuclear magnetic resonance spectroscopy

Fourier-Transform Infrared (FTIR) spectra of monomers and polymers were recorded on Nicolet Avatar 370 spectrophotometer (4000–400 cm^{-1}) using KBr as the matrix. Each spectrum was collected by cumulating 10 scans at a resolution of 4 cm^{-1}. The proton nuclear magnetic resonance (^{1}H NMR) spectroscopy was carried out on a Bruker 300 NMR spectrometer at room temperature. For the monomers, D_2O was used as the solvent. For the polymers, D_2O and $0.5M$ $NaCl/D_2O$ solution were used as the solvents.

Gel permeation chromatography

The number–average MW and MWD of PDMAEMA was determined on a Waters-150 Gel Permeation Chromatography (GPC) system at 25°C, using HPLC-grade THF as eluent at a flow rate of 1.0 mL/min and PS as the standards.

Differential scanning calorimetry

The thermal analysis of PDMABS was carried out on the Perkin–Elmer Pyris-1 differential scanning calorimeter. The sample was heating from 40 to 250°C under N_2 atmosphere, at a heating rate of 20°C/min, after which the sample was cooled rapidly to room temperature and then heated to 250°C at the same rate.

Determination of T_{PT}

T_{PT} was determined in conventional cloud-point approach. Predetermined amounts of PDMAEMA or

PDMABS were added into aqueous media to achieve a specific polymer concentration, in the range from 0.0001 to 0.05 g/mL. HCl, NaOH, and NaCl were used to adjust pH value and ionic strength of aqueous solutions. The aqueous systems were gradually heated by oil bath at a rate of 1–2°C/min until the phase transition occurs; the temperature at which the phase transition occurred was recorded as T_{PT}.

RESULTS AND DISCUSSION

Sulfobetainization of DMAEMA (DMABS)

DMAEMA has a tertiary amine group that could undergo protonation, quaternarization, and betainization.[6,9,10,11,15,19,20] Typical carbobetainizing reagents include lactone, acrylic acid, and haloalkycarboxylate, while sulfobetainizing reagents embrace sultone, vinyl sulfonylchloride, and haloalkysulfonate.[6,9,10,11,15,19,20] In this study, 1,4-butane sultone was chosen to sulfobetainize DMAEMA to produce DMABS. The chemical structure of DMABS was analyzed by FTIR and ^{1}H NMR, respectively.

Figure 1(a,b) show the FTIR spectra of DMAEMA and DMABS. The absorption band at wavenumber of 1635 cm^{-1} was assigned to the C=C double bond. After the betainization, the absorption band at 1165 and 1023 cm^{-1}, associated with the tertiary C—N bond of DMAEMA, disappeared, and a strong absorption of quaternary ammonium appeared at 1043 cm^{-1}; meanwhile, the new absorption band appeared at 1177 cm^{-1}, probably attributable to —SO_3^- groups.

The formation of DMABS was also confirmed by ^{1}H NMR spectroscopy. Figure 2(a,b) show the ^{1}H NMR spectra of DMAEMA and DMABS using D_2O
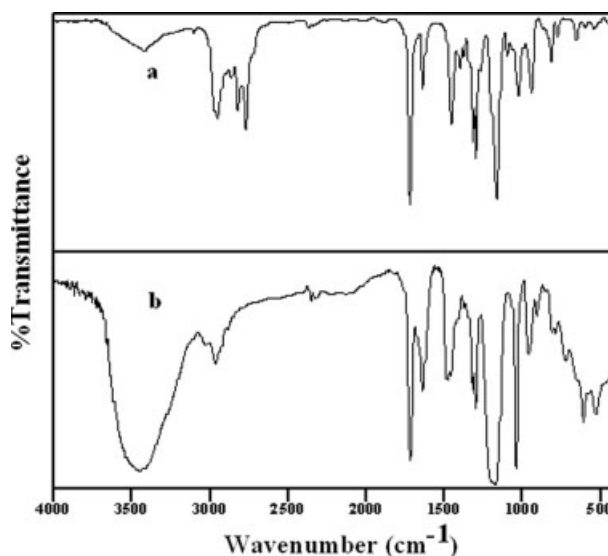

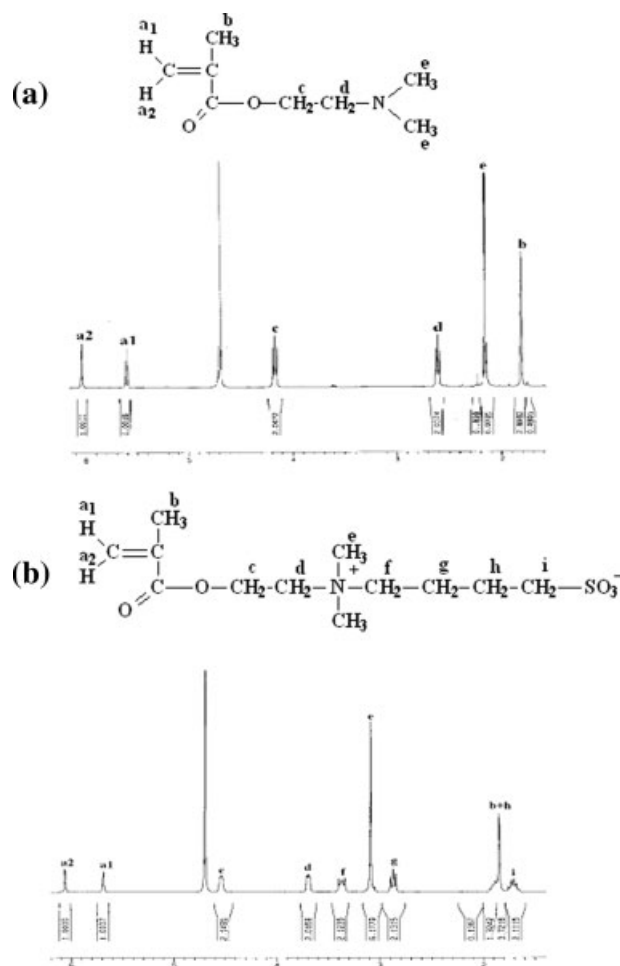**Figure 1** FTIR spectra of (a): DMAEMA (b): DMABS.

Figure 2 ^{1}H NMR spectra of DMAEMA and DMABS.

as solvent, respectively. In common, the peaks at d — 5.7 and 6.1 ppm were assigned to two protons in the CH_2— moieties of both DMAEMA and DMABS, respectively. For the spectrum of DMAEMA, the peaks at d — 1.8, 2.2, 2.6, and 4.2 ppm were assigned to the proton in the $=C—CH_3$ $N—CH_3$, $—CH_2—N$ and $O—CH_2—$ moieties, respectively. The molar ratio of $[CH_2—] : [=C—CH_3] : [O—CH_2—] : [—CH_2—N] : [N—CH_3]$, determined from the integral peak areas, is about $2 : 2.9 : 2 : 2 : 6$, in a good agreement to the theoretical value of $2 : 3 : 2 : 2 : 6$, indicating a high purity of DMAEMA.

For the DMABS, in addition to those associated with the CH_2— moieties, the peaks at d — 1,7, 1.9, 2.8, 3.1, 3.3, 3.7, and 4.5 ppm were assigned to the protons in the $—CH_2—SO_3^-$, $—C—CH_3$, $N^+—CH_2$ $—CH_2—CH_2—$, CH_3N^+, $N^+—CH_2—CH_2—CH_2—$, $O—CH_2—CH_2—N^+$ and $O—CH_2—CH_2$ moieties, respectively. On the basis of the integral peak areas, their molar ratio is well consistent with the theoretical value. Therefore, both the FTIR and NMR results confirmed that DMAEMA was betainized into DMABS.

Electrolyte-responsive conformational dynamics of PDMAEMA and PDMABS

PDMAEMA and PDMABS were prepared via the free radical polymerization. Although DMAEMA is water-soluble, THF, instead, was chosen as solvent to avoid the probable cross-linking. PDMABS was prepared using H_2O as solvent. The apparent number–average molecular weight (MW) and its distribution (MWD) of PDMAEMA were determined by GPC to be about 1.73×10^4 and 1.81, respectively. Because of negligible solubility of PDMABS in THF and the absence of aqueous GPC setup, we failed to determine the exact MW and MWD of PDMABS.

Since PDMAEMA and PDMABS were deemed as weak polyelectrolyte and polysulfobetaine, respectively, it was expected that the ionic strength of the aqueous media could impose significant influence on their chain conformations.[1,19–23] ^{1}H NMR spectroscopy could provide inherent information on the conformational dynamics, as adopted by Bütün,[20] Armes and coworkers,[24] and Einsenberg and co-
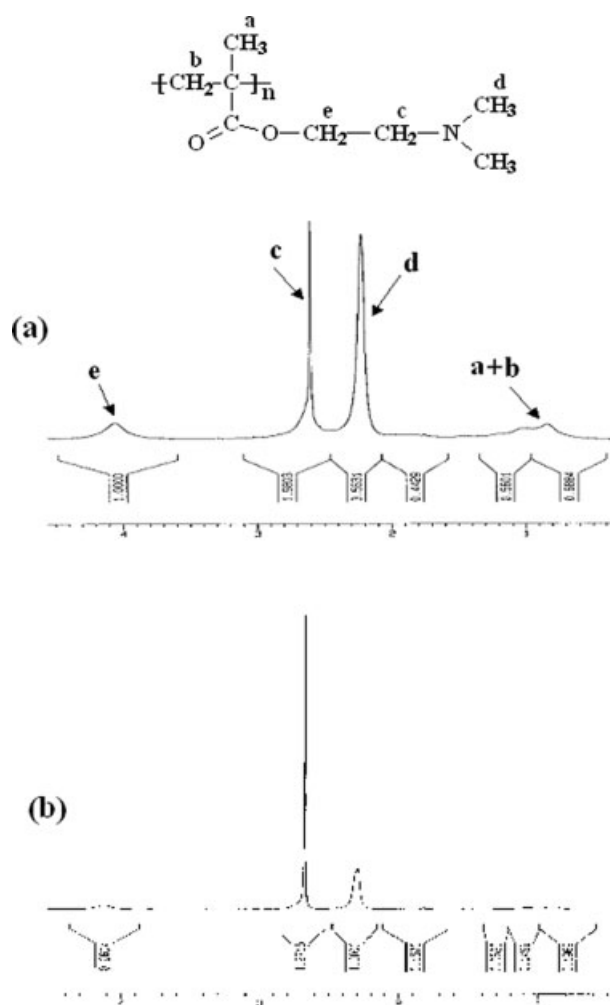

Figure 3 ^{1}H NMR spectra of PDMAEMA: (a) D$_2$O, (b) 0.5M NaCl/D$_2$O.
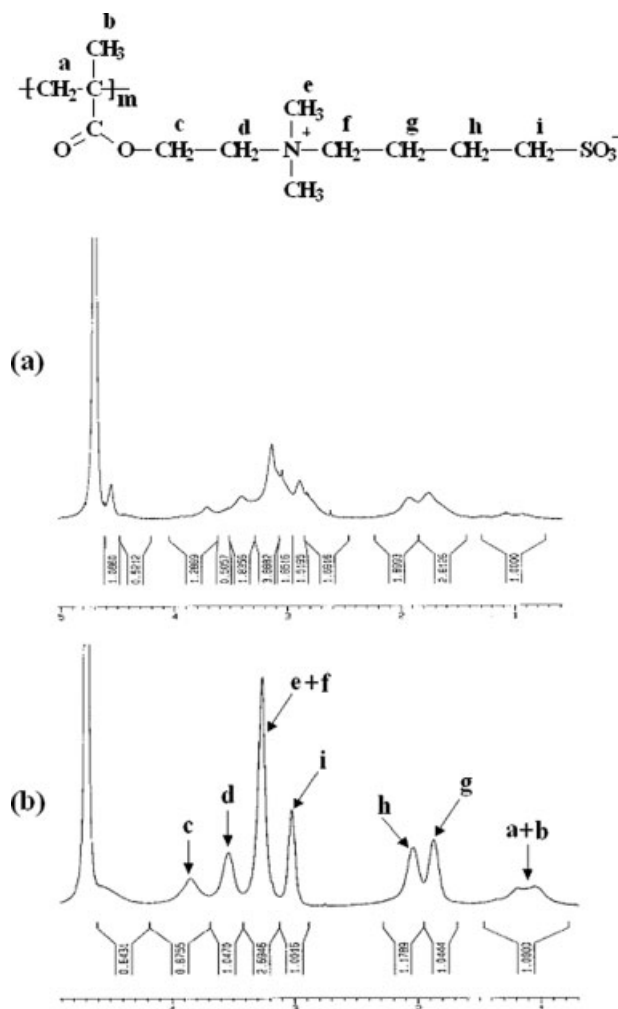
Figure 4 ^{1}H NMR spectra of PDMABS: (a) D$_2$O, (b) 0.5M NaCl/D$_2$O.

workers.[25] In this study, it was used to confirm the chemical structures and conformational changes of the polymers in response to ionic strength.

Figure 3(a,b) show the ^{1}H NMR spectra of PDMAEMA in D$_2$O and NaCl/D$_2$O, respectively. It is discernible that ionic strength holds an important role on the chain conformation; all the intensity of the peaks associated with PDMAEMA chains diminished remarkably with the addition of NaCl. Such a change was attributed to the electrolyte-responsive conformational change of PDMAEMA. The amine moieties of the PDMAEMA chains are partly protonated in D$_2$O, so electrostatic repulsion exists readily, leading to a rather expansive conformation, corresponding to enhanced chain mobility, and thus an enhanced NMR signal intensity.[20,24,25] Upon the addition of NaCl, as stated earlier, the screening effect leads to the collapse of PDMAEMA chain into a compact state, a reduced chain mobility and a reduced NMR signal.

Figure 4(a,b) compare the ^{1}H NMR spectra of PDMABS in D$_2$O and NaCl/D$_2$O, respectively. Com-

paring the figures, the signals appeared much stronger in D$_2$O than in NaCl/D$_2$O. Commonly, it was attributed to the screening effect of small ions to the polybetaine chains. In contrast to PDMAEMA structure, the PDMABS chains contain both cations and anions, among which the electrostatic attraction dominated the intrachain and interchain interaction, so PDMABS chains aggregated into compact globules with significantly restricted chain mobility.[20,24,25] The addition of low molecular weight electrolytes greatly shielded the electrostatic interactions, leading to less restricted chain mobility and an intensified NMR signal. These results further confirmed the low molecular weight electrolytes impose significant influence on the conformational dynamics of PDMABS.

The thermal properties of PDMAEMA and PDMABS were analyzed by differential scanning calorimetry (DSC). Because of the flexible side chains, PDMAEMA homopolymer has a low glass transition temperature (T_g) of about 19°C. Figure 5 shows the DSC curve of PDMABS. For run one, besides a glass transition at about 160°C, the endothermal process steadily occurred at about 80–100°C, attributable to the evaporation of moisture residues. After the thermomechanical history being removed, a T_g of about 175°C was detected. Such a high T_g was primarily due to the presence of zwitterionic side chains, siginificantly improving the intrachain interaction.

Phase transition behavior of aqueous PDMAEMA media

In comparison with those of PNIPAm, PHEMA, PEO, etc., aqueous PDMAEMA media were expected
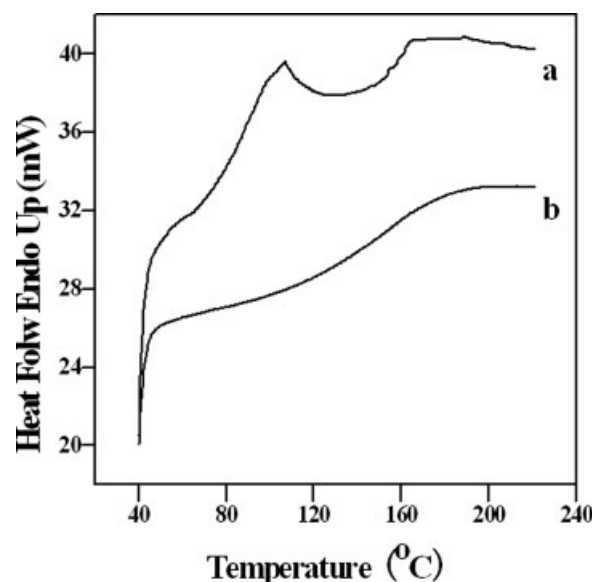

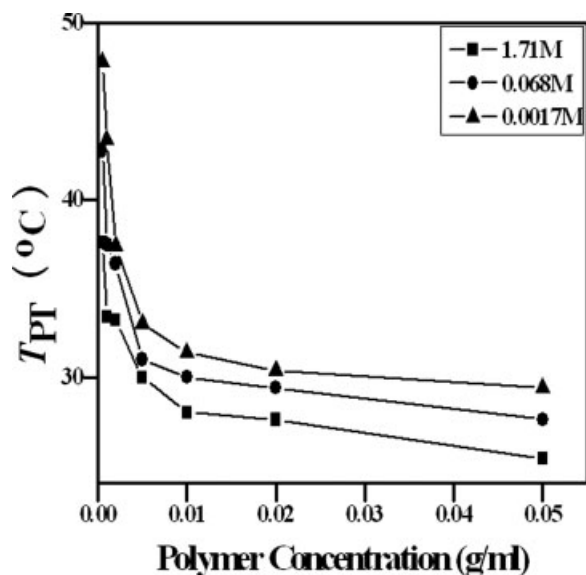**Figure 5** DSC curve of PDMABS: (a) first run and (b) second run.

Figure 6 The dependence of T_{PT} of the aqueous PDMAEMA mixtures on polymer concentration and ionic strength.

to undergo a multidimensional phase behavior in response to temperature, pH and ionic strength in the presence of the amine moieties. In this study, T_{PT} of the aqueous PDMAEMA systems as a function of polymer concentration, ionic strength, pH, etc., was investigated in details.

Figure 6 shows the T_{PT} of the aqueous PDMAEMA systems with different polymer concentration and ionic strength. In common, T_{PT} increased with the decreasing polymer concentration, typical for the LCST-type phase behavior in the dilute regime.[17,18] Because the intrachain and interchain hydrophobic effect in dilute solutions is rather weaker than that in concentrated solution, a higher temperature is required to militate the hydrogen bonding between the PDMAEMA and water, giving rise to a higher T_{PT}.

It could also be observed from Figure 6 that an increase in ionic strength also exerts observable effect on the T_{PT}. As reported for aqueous PNIPAm media,[3] a high ionic strength facilitated the phase transition from solution to emulsion, resulting in a lower T_{PT}. As mentioned earlier, PDMAEMA chain is weakly charged into a weak polycation in water. The electrostatic repulsion among the repeating units drives the PDMAEMA chains to adopt a more extensive conformation. With the addition of NaCl, the repulsion is shielded in such a degree that a more coiled conformation is assumed. As a result, it enables the aqueous PDMAEMA solution of a higher ionic strength to phase separate at a lower temperature. However, it is also noteworthy that such an effect was not sufficiently pronounced, probably ascribable to the low charge density of the PDMAEMA chains.

With PDMAEMA a polybase (pKa of 6.6 or 8),[26] pH plays a pivotal role, via protonation and hydrogen bonding, on the chemical nature, conformational change and phase behavior of aqueous PDMAEMA systems. Figure 7 shows the variation of T_{PT} of the aqueous PDMEMA systems as a function of the medium pH, while the ionic strength and polymer concentration were fixed at $0.1M$ and 0.001 g/mL, respectively. For the solution with a pH < 3, no phase transition was observed to occur. Clearly, in highly acidic media, PDMAEMA units are highly protonated, giving rise to a cationic polyelectrolyte chains. The electrostatic repulsion has overcome the contractive potential induced by hydrophobic interaction among the backbones. For the solvent with a pH of 3, the mixture exhibited a T_{PT} of 54°C, indicating a fact that because of a low proton concentration, much less repeating units were protonated so that the hydrophobic interaction outweighed the electrostatic repulsion and the hydrogen bonding, giving rise to a phase separation at elevated temperature.

Similarly, with pH increasing to 4 and 5, respectively, T_{PT} was detected to be about 34°C and 33°C, respectively. With pH shifting from neutral to alkaline, the T_{PT} of the aqueous PDMAEMA mixture was about 30–31°C, approximately independent on the solvent pH. To the extreme, when the medium pH was adjusted to 13, PDMAEMA cannot be well dissolved to form a homogenous solution even at room temperature, indicating that the hydrophobic interaction has dominated the intramolecular and intermolecular interaction, or, in other words, the hydrogen bonding has been too weak to well solubi-
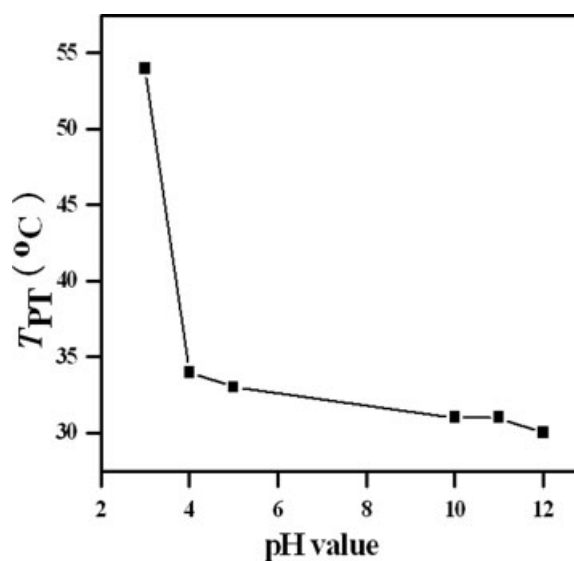

Figure 7 The dependence of T_{PT} of the aqueous PDMAEMA mixtures on pH; ionic strength and polymer concentration fixed at 0.1 mol/L and 0.0001 g/mL, respectively.
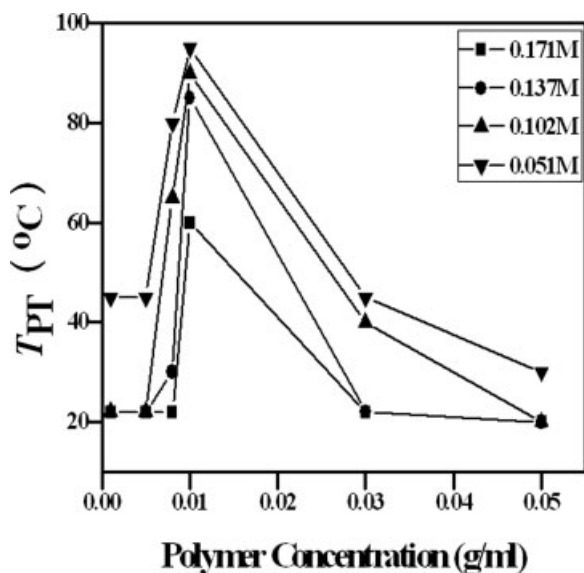
Figure 8 T_{PT} of aqueous PDMABS system with different ionic strength and polymer concentration.

lize the PDMAEMA in the aqueous media at room temperature.

Phase transition behavior of aqueous PDMABS systems

Aqueous polybetaine systems form heterogeneous emulsions at lower temperature. Upon heating or adding NaCl, as a result, the systems undergo a phase transition to homogenous solution. It has been also reported that the phase behavior of aqueous polybetaine systems also depends on polymer concentration, ionic strength, pH, etc. Therefore, a series of experiments were conducted to correlate these factors.

Effects of ionic strength

In our study, the aqueous PDMABS system maintained turbid even when the system was heated close to about 100°C. Besides, for the systems with a higher PDMABS load, PDMABS failed to be well dispersed during short period. Thus, NaCl was added into the system to adjust the ionic strength, and the polymer concentration was set at 0.001–0.05 g/mL.

Figure 8 shows T_{PT} of aqueous PDMABS system as a function of polymer concentration and ionic strength. In general, the addition of NaCl led to an obvious decrease in T_{PT}, a typical behavior associated with the anti-polyelectrolyte effect. On the other hand, the polymer composition exerted a dual influence on T_{PT}. In the dilute regime, the increase of the polymer concentration gave rise to a remarkable increase in T_{PT}. Nonetheless, after achieving a maxi-

mum at a polymer concentration of about 0.01 g/mL, T_{PT} decreased steadily with the further increase in the polymer concentration. Such a parabolic change in T_{PT} with respect to the polymer concentration indicates that, for the systems studied in this section, their UCST might approximately equal to T_{PT} at a polymer concentration of 0.01 g/mL.

Figure 9 shows the variation of UCST, as derived earlier, of these systems as a function of ionic strength of the aqueous media. In contrast to the aqueous PDMAPS mixture,[14] it is evident that an increase in ionic strength could lead to a significant decrease in UCST of the aqueous PDMABS system. For example, an increase in ionic strength from 0.051 to 0.137M, corresponds to a steady decrease in UCST from 95 to 85°C. Furthermore, an increase in ionic strength to 0.171M led to a significant decrease of UCST to 60°C. What is more, in our study, a further increase in ionic strength may result in a UCST below room temperature; i.e. the aqueous PDMABS systems with any PDMABS load and ionic strength higher than 0.2M, could maintain homogeneous and transparent, even at room temperature. On the other hand, the decrease in ionic strength would enhance the UCST of the aqueous PDMABS system adversely. In our study, heating these mixtures with very low ionic strength to even about 100°C failed to obtain a highly transparent solution.

Effect of pH value

It has been believed that since sulfonic acid is a strong acid, no hydrolysis or association occurs for aqueous polysulfobetaine systems. Consequently, pH-sensitive properties could only exist in aqueous
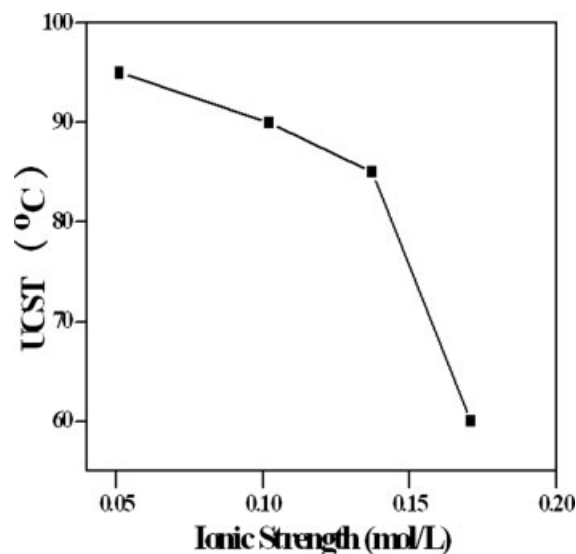

Figure 9 The dependence of UCST of aqueous PDMABS systems on ionic strength.
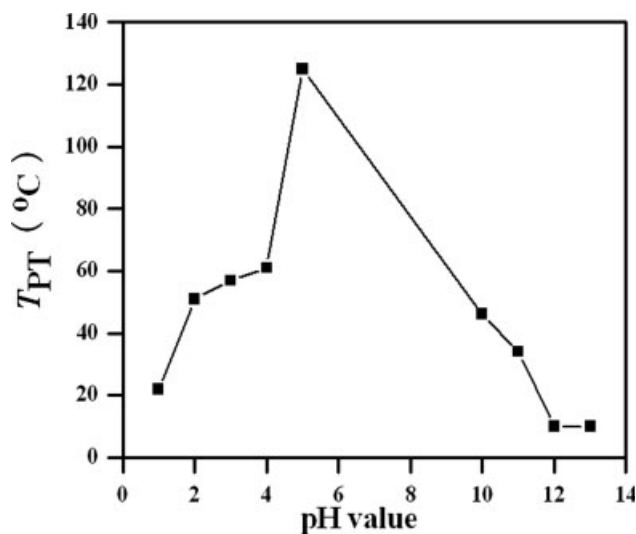
Figure 10 The dependence of T_{PT} of the aqueous PDMABS mixtures on pH; ionic strength and polymer concentration fixed at 0.1 mol/L and 0.0001 g/mL, respectively.

polycarbobetaine systems and it was absent, or rather weak at least, in aqueous polysulfobetaine systems.[9–11,15] However, Armes, McCormick et al. have systematically investigated the pH-sensitive properties of aqueous polybetaine systems. It was revealed then that even aqueous polysulfobetaine systems can exhibit a series of pH-sensitive solution properties.[23,24,27] In this section, the T_{PT} of aqueous PDMABS systems was correlated to the solvent pH at a fixed polymer concentration and ionic strength.

Figure 10 shows the dependence of T_{PT} of aqueous PDMABS systems on medium pH, with polymer concentration and ionic strength fixed at 0.001 g/mL and 0.1M, respectively. In acidic or basic media, the mixtures could be homogenized into transparent solutions upon heating to slightly above temperature. In general, with the medium pH shifting to the neutral range, T_{PT} increases gradually. For example, T_{PT} achieved a maximum up to 125°C in a medium with pH of 5.

Such a pH-sensitive T_{PT} variation was probably attributed to the site-binding ability of ammonium and sulfonate ions. Although the protonation of sulfonate anions is rather difficult.[9,10,15] in acidic media, a high proton concentration renders it possible that protons, replacing ammonium cations, preferably diffuse into the vicinity of sulfonate anions, resulting in a militated electrostatic attraction. In the highly basic media, hydroxide anions exclude the sulfonate anions close to ammonium cations. In the neutral media, both proton cations and hydroxide anions are sparsely dispersed, rarely reducing electrostatic attraction. As a result, the intrachain and interchain electrostatic attraction reached the maximum, which needs a higher medium temperature to disrupt.

CONCLUSIONS

T_{PT} of various aqueous mixtures of PDMAEMA and PDMABS, as two multidimensional stimuli-responsive water-soluble polymers, were determined as a function of polymer concentration, pH and ionic strength to study their LCST- and UCST-type phase transition behaviors, respectively.

For aqueous PDMAEMA systems, a decrease in polymer concentration leads to a higher T_{PT} in the dilute regime while a higher ionic strength promoted the phase separation at lower T_{PT} probably due to the polyelectrolyte effect. pH directly controlled the solubility of PDMAEMA. In highly acidic media, the electrostatic repulsion retards the conformational contraction; a gradually militated protonation gave rise to a steady decrease in T_{PT} to even below room temperature.

Aqueous PDMABS mixtures exhibited classical UCST-type phase transition behaivor. Their UCST decreases monotonically with the increase in ionic strength of the aqueou media because of anti-polyelectrolyte effect. The phase transition behavior of aqueous PDMABS systems also showed a pH-dependent character: T_{PT} achieved a maximum in the neutral media and decreased significantly when the media shifted to highly acidic or basic. Such a pH-dependent variation was attributed to the site-binding ability of ammonium and sulfonate ions, respectively.

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